# PREDICTING STABILITY AT THE REFINERY USING SMORS

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## INTRODUCTION

It has been previously reported[1] that extraction with methanol will improve storage stability characteristics for mid distillate diesel fuel which is at least 6 months old. Moreover, a potential relationship between the methanol soluble, hexane insoluble extractible material and the thermally induced precipitate (TIP) which forms in some fuels under accelerated aging conditions which simulate long term ambient storage, has been suggested.[2,3] Fuel stability is currently assessed through the use of an accelerated aging procedure.[4] However, the procedure or procedures used require substantial commitments of laboratory time and resources and they are necessarily limited to predicting only the relatively short term (1 - 2 years). A predictive stability test which could serve for field use for fuels at least 6 months old, or which would require a sufficiently short turnaround time to make it attractive for procurement use is highly desirable. This is particularly true when circumstances require that the fuels may be stored for very extended periods, such as military fuel reserves.

Fuels which have been aged by six months of ambient storage in the laboratory or field show a very linear relationship between the solids produced by methanol extraction and subsequent precipitation with hexane (EIP - extraction induced precipitate), and solids, or insolubles, formed during the stress, or accelerated aging process (TIP).[3] Thus, for these fuels, the extractibles yields can be used as a predictive test for storage stability. When these aged and thermally stressed fuels are extracted with methanol after filtration for TIP, the yield of extractible solids is typically found to be no more than a few percent higher than the EIP isolated from the unstressed fuel. We propose that, for those cases where the post-stress extractibles (PEIP) yields are about equal to the pre-stress yields (EIP), there is an equilibrium concentration of distributed soluble macromolecular material (which we have previously called SMORS).[2,3,5,6] Examples of fuels which have been aged to this equilibrium condition are found in Table 1 (Code A = aged).

Fuels which are refinery fresh, or are not aged to equilibrium either because they have been stored under non-oxidative conditions (inert atmosphere, freezer conditions) or their ambient storage times are too short, will frequently show very different extractibles yields before and after accelerated aging. Until these fuels are aged to equilibrium there is no consistently useful relationship between EIP and TIP to obviate the need for a stress test. Some examples of pre (EIP) and post (PEIP) stress extractibles yields for some fresh fuels are also found in Table 1 (Code F = fresh).

Because accelerated aging tests for new fuels do not generally permit storage stability prediction beyond a year or so under ambient conditions and because they are not always reliable, we are suggesting that a stress test in combination with a post stress determination of extractibles will serve to better identify fuels which are likely to develop undesirable storage characteristics over time. This test could serve as the basis for deciding which fuels could be safely stored for additional extended periods, and which should be used promptly. We also provide additional experimental evidence to link the extractible material (SMORS) with insoluble sediment formed as a result of ambient storage.

## EXPERIMENTAL

The fuels used in this work were refinery fresh fuels which were tested for EIP and TIP (insolubles) as soon as they reached the Laboratory. They included two light cycle oil (LCO) stocks and two straight runs (SR). For experimental purposes, the fuels tested were the two LCOs and 80%/20% blends of the SR/LCO pairs. Designations for the experimental fuels are found in Table 2.

All fuels involved were tested for pre and post stress extractibles (EIP/PEIP) as soon as they were received and at later intervals, ranging between one and nine months, as well. They were tested for insolubles using the 16 hour ASTM D 5304 - 92 procedure at those same times. All fuel aliquots were prefiltered through two thicknesses of 0.8u 47mm nylon filters (MSI, Westboro,MA) using a water aspirator. Aliquots were 100 mL each; separate aliquots were used for the EIP and for the TIP/PEIP determinations. Stress conditions were 16 hrs., 90°C, 690 kPa oxygen overpressure. Post-stress samples were first filtered for TIP, then subjected to extraction for the determination of PEIP.

For the insolubles (TIP) determination: samples were filtered using glass fiber filters and the procedure described in detail elsewhere.[4] For the extractibles determinations: prefiltered aliquots were extracted (separatory funnel; shake 90 sec.) with 40 mL reagent grade methanol. The methanol phase was rotary evaporated for 30 minutes at 58-63°C. After cooling, 50 mL of reagent grade hexane was added to induce precipitation. The resulting precipitate was filtered (nylon filters) and dried at 70°C for at least 20 minutes to remove any traces of hexane before weighing.

An experimental series was performed to test possible effects of a tertiary alkyl amine stabilizer additive on insoluble sediment (TIP) formation and on post stress extractibles (PEIP) formation. The amine additive has been tested in this laboratory and elsewhere and is known to reduce insolubles formation in some fuels.[7] Light cycle oil samples (Fuels B, D) were doped with the additive in varying concentrations (6 - 890 ppm w/v) and tested, along with control samples, using the same procedures previously described for the TIP and PEIP determinations. All samples were run in duplicate and the aliquot size was 100 mL.

## RESULTS AND DISCUSSION

### Aging (Stress) and Extractibles Testing

Table 3 provides a summary of ambient storage times, pre- and post-stress extractibles levels (EIP and PEIP) and total insolubles/100 mL following the standard 16 hour LPR test (ASTM D 5304 - 92). Fuel A, tested at monthly intervals from 1-3 months passes the LPR test (current pass/fail criterion is 3 mg/100 mL). Pre- and post-stress extractibles levels indicate no tendency for the fuel to degrade over time with respect to insolubles formation and suggest this fuel could be safely stored for extended periods. Fuel B is a light cycle oil and thus might be considered a potential "worst case" fuel. During the time interval between 0 and 3 months of ambient storage the fuel passes the LPR test. The pre-stress extractibles are low, but the post-stress extractibles are increasing to the point where their level suggests that this fuel is not a candidate for long term storage. By 8.5 months of ambient storage LPR insolubles (TIP) and extractibles levels have increased to the point where they support an argument for prompt use. In particular, the post-stress insolubles yield has increased to a level which suggests the fuel is likely to deteriorate badly in the near term. Also EIP and PEIP are beginning to approach equilbrium.

Fuels C and D are an interesting pair; fuel D being a light cycle oil and C a blended fuel comprised of 20% D and 80% straight run stock. Fuel D fails the LPR test badly on initial testing. Moreover, the post-stress extractibles level (41 mg/100 mL) is high and supports the conclusion that this is an unstable fuel. As time passes and the fuel is subjected to ambient storage conditions, the condition of the fuel actually improves as noted by TIP (ASTM D 5304) and PEIP (or post-stress extractibles) levels. Note that this LCO, even at 6 months, is not aged to equilibrium and so pre-stress extractibles levels are not as effective predictors of future behavior as are the post-stress levels. By 12 months of ambient storage the fuel has improved to where it passes the LPR. The PEIP has declined as the pre-stress extractibles level has increased. If the existing extractibles (EIP) are subtracted from the PEIP one obtains a measure of the "aging tendency" during the stress test. For this LCO the trend is toward improvement. The relationship between TIP and PEIP formed during accelerated aging is striking: at 0 months of ambient storage TIP is 8.3 mg/100 mL and PEIP is 40.9 mg/100 mL; at 12 months the numbers have fallen to 1.6 and 13.8 mg respectively.

Fuel D is an unusual LCO in that its storage stability with respect to insolubles formation improves as it ages under ambient conditions. However, if criteria we have proposed for aged LCOs using a 24 hour modification of the LPR stress test (TIP $\geq$ 6 mg/100 mL; extractables $\geq$ 32 mg/100 mL)[3] are adapted to the 16 hr test, predictions for future storage behavior can be made. Based on post-stress extractibles yields (which must be used rather than pre-stress yields until the fuel is aged to equilibrium) we would predict that, at equilibrium, the pre- and post-stress yields would be roughly equivalent. This fuel is clearly "limited" with respect to the total insolubles it can form during its lifetime prior to use. It apparently forms insolubles rapidly, then levels out to become a rather benign fuel with respect to continued insolubles formation. While this fuel obviously improves with age, it is not a suitable candidate for procurement on the basis of its poor initial extractibles/aging tests. Moreover, even if it were to be held in storage to equilibrium, there would be so much particulate matter suspended in this fuel as to present filtration problems. Thus, this fuel is not a candidate for procurement. Fuel C, the blended stock, is a likely storage candidate on the basis of its extractibles and TIP yields. On the basis of its consistent PEIP and stress test behavior and on its fuel D LCO content, this fuel appears to be a suitable candidate for storage and makes a case for safe storage and use of cracked stock blends.

## Effect of Additives

Tables 4 and 5 present results obtained for the two light cycle oils that were tested with the tertiary amine additive (additive #1). Fuel B was also tested using another additive, a hindered phenol (additive #2), for purposes of comparison. Table 4 summarizes additive testing for fuel B. Insolubles (TIP) formation tendency for this fuel is not reduced with either additive. Indeed, it might be argued that TIP increased somewhat on addition of the tertiary amine. PEIP yields for all samples were comparable. Thus, fuel B appears to be one of those fuels that is not affected by tertiary amine additive treatment.

Fuel D, on the other hand, is responsive to additive #1. As was the case with fuel B, additive #2 had no effect on this fuel. Table 5 shows the reduction in insolubles (TIP) that occurs when fuel D is subjected to the 16 hour LPR test after treatment with varying levels of additive #1. A corresponding decrease in PEIP levels is also observed. The fact that additive #1 reduces PEIP levels as it reduces TIP provides additional evidence for a relationship to exist between extractibles levels and the tendency toward insoluble sediment formation in diesel fuels.

## Summary

A relationship between extractibles levels before (EIP) and after (PEIP) accelerated aging and insolubles formation tendency has been found to exist in fuels that have not been aged to EIP/PEIP equilibrium. Additional evidence for the relationship between these entities has been provided by the comparable effect of a common stability additive on post stress extractibles and insoluble sediment. Thus, we propose that a combination of the LPR (ASTM D 5304) stress test and methanol extraction of the filtered, stressed fuel with subsequent precipitation of the hexane insoluble fraction, may serve as a basis for a predictive test for storage stability. This test would enable better decisions to be made as regards the candidacy of fuels for long term storage as opposed to their candidacy for prompt usage. Moreover, for cases where storage is required, this test combination might serve as a reasonable basis for procurement.

References

1. Wechter, M. A., and Hardy, D. R. 1989. The Isolation of Precursors Responsible for Insolubles Formation in Mid-Distillate Diesel Fuels. Fuel Science and Technology Intl., 7, 423.

2. Hardy, D. R. and Wechter, M. A. 1990. Insoluble Sediment Formation in Middle-Distillate Diesel Fuel: The Role of Soluble Macromolecular Oxidatively Reactive Species. Energy and Fuels, 4, 270.

3. Wechter, M. A. and Hardy, D. R. 1991. The Use of Soluble Macromolecular Oxidatively Reactive Species (SMORS) to Predict Storage Stability of Mid Distillate Diesel Fuels. Proceedings of the Fourth International Conference on Stability and Handling of Liquid Fuels, U.S. Department of Energy, 4, 620.

4. ASTM D 5304 - 92. Standard Test Method for Assessing Distillate Fuel Storage Stability by Oxygen Overpressure. American Society for Testing and Materials, Annual Book of ASTM Standards, Vol 05.03.

5. Hardy, D. R, and Wechter, M. A. 1990. What are Soluble Macromolecular Oxidatively Reactive Species (SMORS)? Preprints of the Division of Fuel Chemistry, American Chemical Society, 35, 1176.

6. Hardy, D. R. and Wechter, M. A. 1994. Characterization of Soluble Macromolecular Oxidatively Reactive Species (SMORS) from Middle Distillate Diesel Fuels: Their Origin and Role in Instability. Energy and Fuels, In Press.

7. Hazlett, R. N., Hardy, D. R., White, E. W. and Jones-Baer, L. 1985. Assessment of Storage Stability Additives for Naval Distillate Fuel. SAE Technical Paper Series, 851231, Washington, D.C.

Table 1. Weight of Solids Isolated from the Pre- and Post-Stress Hexane-Insoluble Fraction of the Methanol Extracts of Five Aged and Three Fresh Light Cycle Oil Diesel Fuels[a]

| fuel code | EIP: mg/100 mL | PEIP: mg/100mL | aged,A or fresh,F |
|---|---|---|---|
| LCO-1 | 112 | 116 | A |
| LCO-2 | 14 | 17 | A |
| LCO-3 | 53 | 63 | A |
| LCO-4 | 27 | 40 | A |
| LCO-5 | 92 | 114 | A |
| LCO-12 | 1 | 14 | F |
| LCO-13 | 2 | 101 | F |
| LCO-14 | 2 | 58 | F |

[a]Storage stress test was for 24 h at 90°C and 690 kPa of oxygen.

Table 2. Experimental Fuel Designations.

| Fuel | Type | Legend |
|---|---|---|
| A | Blend | 80% 91-34(SR)+20% 91-35(LCO) |
| B | LCO | 100% 91-35(LCO) |
| C | Blend | 80% 92-1(SR) + 20% 92-2(LCO) |
| D | LCO | 100% 92-2(LCO) |

Table 3. Summary of Test Fuel Results

| fuel | Months of Storage time (ambient) | TIP (mg/100mL) | EIP (mg/100mL) | PEIP (mg/100mL) |
|---|---|---|---|---|
| A | 0 | 1.3 | 0.23 | 0.16 |
| A | 1 | 0.4 | 0.05 | 0.26 |
| A | 2 | 0.8 | 0.3 | 2.5 |
| A | 3 | 0.7 | 0.6 | 2.5 |
| B | 0 | 1.9 | 0.29 | 6.8 |
| B | 1 | 1.3 | 0.17 | 7.8 |
| B | 2 | 1.6 | 0.3 | 12.5 |
| B | 3 | 1.9 | 2.3 | 28.1 |
| B | 8.5 | 2.3 | 5.0 | 45.8 |
| B | 14 | 1.4 | 13 | 34.6 |
| C | 0 | 1.8 | 0.09 | 6.6 |
| C | 0.5 | 2.2 | 0.15 | 5.4 |
| C | 1.5 | 2.5 | 0.7 | 5.6 |
| D | 0 | 8.3 | 0.22 | 41.1 |
| D | 0.5 | 7.6 | 0.19 | 40.6 |
| D | 1.5 | 5.2 | 2.1 | 28.0 |
| D | 6 | 4.4 | 7.3 | 34.9 |
| D | 12 | 1.6 | 16.2 | 30 |

Table 4. Additive studies for fuel B at 8.5 months ambient storage

| Sample tested | mg TIP | mg EIP | mg PEIP |
|---|---|---|---|
| Fuel | 2.3 | 5.0 | 48.8 |
| Fuel + 24ppm #1 | 3.3 | - | 39.3 |
| Fuel + 24ppm #2 | 2.5 | - | 42.6 |
| Fuel + 24ppm # 1,2 | 3.2 | - | 47.2 |

Table 5. Studies for fuel D at 6 months ambient storage using additive #1.

| Sample tested | TIP | EIP | PEIP |
|---|---|---|---|
| Fuel | 4.4 | 7.3 | 34.6 |
| Fuel + 6ppm | 1.3 | - | 17.5 |
| Fuel + 24ppm | 1.1 | - | 16 |
| Fuel + 890ppm | 1.7 | - | 22.6 |